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REVIEW OF GRUMMAN STUDIES  
IN METAL SOLIDIFICATION

November 1971

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Normal Freezing Equations  
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Segregation Ratio

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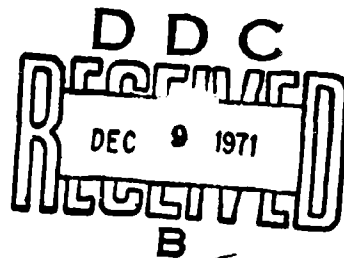
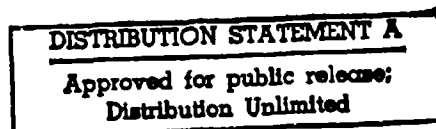
REVIEW OF GRUMMAN STUDIES  
IN METAL SOLIDIFICATION

by

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Materials and Structural Mechanics Section

November 1971



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## DISCUSSION

Metals solidification has been observed and practiced for thousands of years, but has been systematically studied only over the past several decades. Only since the beginning of the semiconductor industry has metal solidification been more rigorously and quantitatively investigated. This is because even ppm of wanted or unwanted impurities can radically change the characteristics of such devices. Today we recognize the significance of small amounts of impurity in all materials, including structural materials. A comprehensive review on metals solidification is given by Chalmers in Ref. 1.

Normal Freezing - A very useful equation employed in the field is the linear normal freezing equation that approximates the liquidus and solidus curves by two straight lines. This equation is so important in materials processing that it has been repeatedly derived (Refs. 2-10). This equation is  $c = kc_0(1-g)^{k-1}$ , where  $c$  is the solute concentration in the frozen solid at fraction  $g$  solidified,  $c_0$  is the initial solute concentration in the melt, and  $k$  is the constant segregation coefficient.

Nonlinear Normal Freezing - In the study of granular, cellular, or dendritic growth, the above linear equation can also be used in the initial stages of solidification, where both  $g$  and the solidification range are not too large and  $k$  is fairly constant but, unfortunately, where the probing work is least productive, as will be shown. On the other hand, in many metallurgical applications, this is not the case. In particular, the last solidifying portions at the grain, cell, or dendrite boundaries are often critical in determining the mechanical, electrical, and other properties of the frozen material (Refs. 11-14). Yet a moderate or very wide solidification range (down to the eutectic temperature) and, hence, curved liquidus and solidus lines must be dealt with. The value of  $k$  is then definitely nonconstant. The above linear normal freezing equation is now not applicable and can even be misleading (Refs. 15-16). Normal freezing equations for cases where the liquidus and solidus curves are quadratic, cubic, or higher degree functions of the melt temperature, or are logarithmic functions of the reciprocal absolute melt temperature (i.e., ideal solutions), have been solved in closed forms and published previously (Refs. 11, 17, 16, 18). The normal freezing equation for ideal binary solutions (Ref. 18) presents the interesting possibility of computing, with the minimum of experimentation and without the use of phase diagrams, of the solidification behavior or frozen solid concentration profile, directly from some basic thermodynamic quantities. In addition,

computer programs, known to give results accurate to ppm compared to exact solution results, have been worked out to handle numerically any solidification problems with any phase diagram (Ref. 19). These equations and computer programs should be used in such metallurgical applications.

Examples of the uses of these equations and programs have been described in some detail relative to general metals solidification (Ref. 20), single crystal growth (Ref. 21), cellular growth (Ref. 22), granular growth (Ref. 23), and zone melting (Ref. 24).

The value of these equations and programs can be seen also from the following. At the centers of grains, cells, and dendrites,  $g$  is small and the linear freezing equation is sometimes a good approximation. The changes in solute concentration with distance, i.e.,  $dc/dg$  or  $dc/dx$ , in these central areas are, however, relatively slow and small, as can be seen in Fig. 1 of Ref. 25 and also by taking derivatives on the various normal freezing equations. For a given spot size examined by the electron microprobing technique, therefore, the information content on the solute per spot is minimal. On the other hand, at or near the boundary regions of grains, cells, or dendrites, the changes in solute concentration from spot to spot are large, i.e., the information density is highest, yet, the linear freezing equation is distinctly inapplicable, as discussed above and in Refs. 15-17, 26.

Thus, we believe our equations and computer programs for studying solidification are the only ones that are valid and effective at these boundary regions where it is most informative and fruitful to probe. We will extensively use these equations and programs in our future work on solidification.

Meaning of the Segregation Ratio - In this connection, we have studied the conventional methods of microprobing during the investigation of melt solidification and purification or solute segregation. In particular, we have carefully examined the commonly used criterion of segregation, i.e., segregation ratio (defined as the maximum solute concentration to the minimum across the grain, cell, or dendrite). Our conclusion is that the meaning of this ratio generally is not fully understood and that this ratio is always more or less underestimated (Ref. 25). As a result, the measured segregation ratios vary not only with growth rate, liquid temperature gradient, and initial solute concentration, but also with grain, cell, or dendrite size; or even from sample to sample, equipment to equipment, and investigator to investigator (Ref. 27). In a word, these measured ratios are not reproducible. We have developed a new boundary region model that qualitatively explains many of these observed variations in segregation ratios (Ref. 25). Quantitative study of these same variations is under way (Ref. 19).

Eddy and Convection Currents in Melt - In metal solidification, gravity effects are often significant. In fact, gravity-induced convection currents in the liquid melt often markedly affect melt mixing. Other types of convection currents also may exist. A temperature gradient across the molten drop, for example, causes a surface tension gradient leading to surface mass flow and internal convection currents. This same temperature gradient will also yield a vapor pressure gradient causing internal mass flow and convection currents. A temperature gradient must also cause a solute concentration gradient (because of varying liquid and solid solubilities with temperature). This concentration gradient gives rise to a surface tension gradient and again, convection currents, because the surface tension is usually a function also of the solute concentration.

Solidification with Variable-k and Limited Liquid Diffusion - All of these convection currents or eddy currents, together with any other types of agitation such as arise from mechanical or electromagnetic stirring, always increase the liquid diffusion. Our work on solidification with limited liquid diffusion and variable segregation coefficient (Ref. 26) is particularly pertinent here. In this work, the Tiller-Jackson-Rutter-Chalmers equation (Ref. 28) for normal freezing with constant-k and limited liquid diffusion has been modified to account for curvatures of the liquidus and solidus lines on the phase diagram, that is, the segregation coefficient is now allowed to vary with the melt temperature and solute concentration. The resultant, closed-form equations show that even under steady-state conditions, the effective segregation coefficient, the relative solute concentration profile in the interfacial diffusion layer and, hence, the degree of supercooling for a given liquid temperature gradient, vary with the initial solute concentration. These results are in contrast with Tiller-Jackson-Rutter-Chalmers predictions. The improved results should more accurately predict the actual degree of constitutional supercooling, the melt nucleating characteristics, the morphological transition of the grown crystals, and the complete melt solidification behavior. Computed results from both sets of equations have been presented and compared for some binary alloy systems with variable initial solute concentrations, on such parameters as steady-state interfacial concentration profiles and critical liquid temperature gradient for transition from macroscopically planar into the cellular growth pattern. The effective segregation coefficient, and the effective width of the diffusion layer  $\delta$  can be similarly determined by a modified equation and a modified log-log plotting procedure, respectively (Ref. 26).



Figure 1, taken from Ref. 26, shows that for the steady-state growth of Al-Cu under a given liquid temperature gradient  $G$ , the critical growth velocity  $v_c$  (i.e., the maximum growth velocity without causing constitutional supercooling and nonplanar growth), depends markedly on the initial copper concentration  $c_0$ . Also, the critical growth velocity  $v_c$  is universally overestimated by Tiller et al. Further, the overestimation is alarmingly great for  $c_0$  below about  $10^{-4}$  (100 ppm) and particularly above  $10^{-2}$  (1%). This also means that in most Al-Cu growth, the equation of Tiller et al. (Ref. 28) gives critical growth rates that, if followed, must unexpectedly give cellular or even dendritic growth rather than the desired planar, single crystal growth. Thus, Ref. 26 shows that both the variable segregation coefficient and limited liquid diffusion must generally be considered. Neglecting either may introduce serious errors. Yet such types of solidification study involving both variable segregation coefficient and limited liquid diffusion seem to be absent in the open literature.

Surface Evaporation - Another factor in metal solidification that deserves serious consideration is the phenomenon of vacuum evaporation. While the vapor pressure and evaporating rates for various metals at different temperatures have been given (Ref. 29), similar data on alloy evaporation are almost nonexistent. We have solved the differential equation relative to the behavior of alloy evaporation and published the equation and its solution in Ref. 11. In this article we pointed out that in the evaporation of an alloy drop, not only is the evaporating alloy volume and surface area constantly decreasing, but the alloy composition is continuously changing due to evaporative solute segregation. Using our evaporation models, equations, and computer programs, we have been able to compute the time to reach a certain drop size or weight, and drop or deposit composition. Figure 2 shows the results of such computations for the case of a Ge-Au levitated sphere suspended in vacuum, or molten hemisphere on an inert heater. The molten drop has an initial Au concentration,  $c_0$ , of 100 ppm and a diameter,  $d_0$ , of 0.3 cm, and is evaporating at 1800°K from the spherical or hemispherical surface. This illustration shows that the alloy drop decreases in diameter by 10 percent (from 0.3 to 0.27 cm) in about 138 seconds, and by 50 percent in 690 seconds, while the solute Au concentrations in the deposit are 134 and 44.1 ppm at the end of these time intervals. We have presented other work on some special aspects of alloy evaporation, e.g., evaporation time and optimum evaporation temperature to achieve given purification results (Ref. 30).

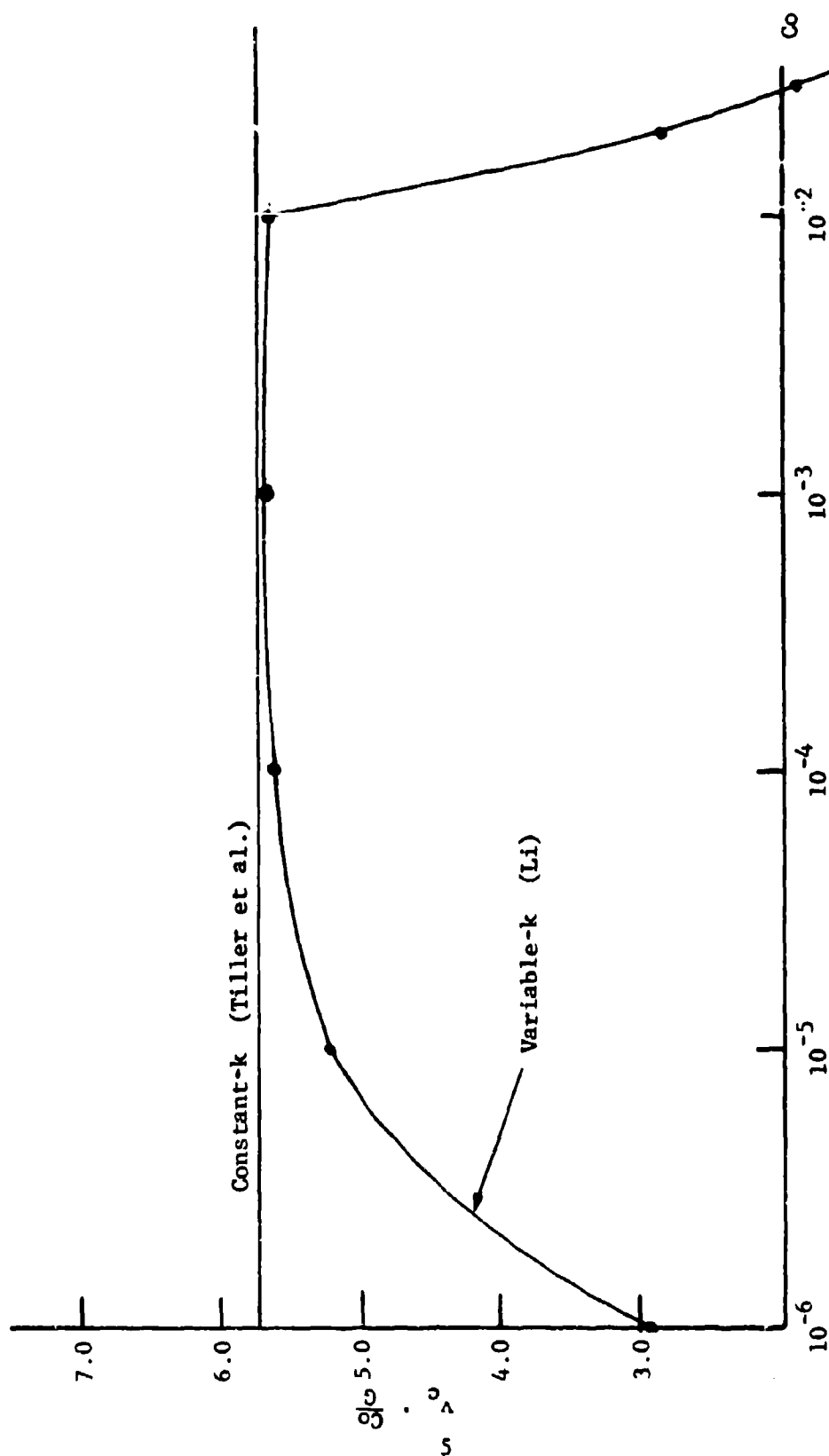


Fig. 1 Critical Growth Velocity for the Al-Cu Solidified under Limited Liquid  
Diffusion, with Constant and Nonconstant  $k$

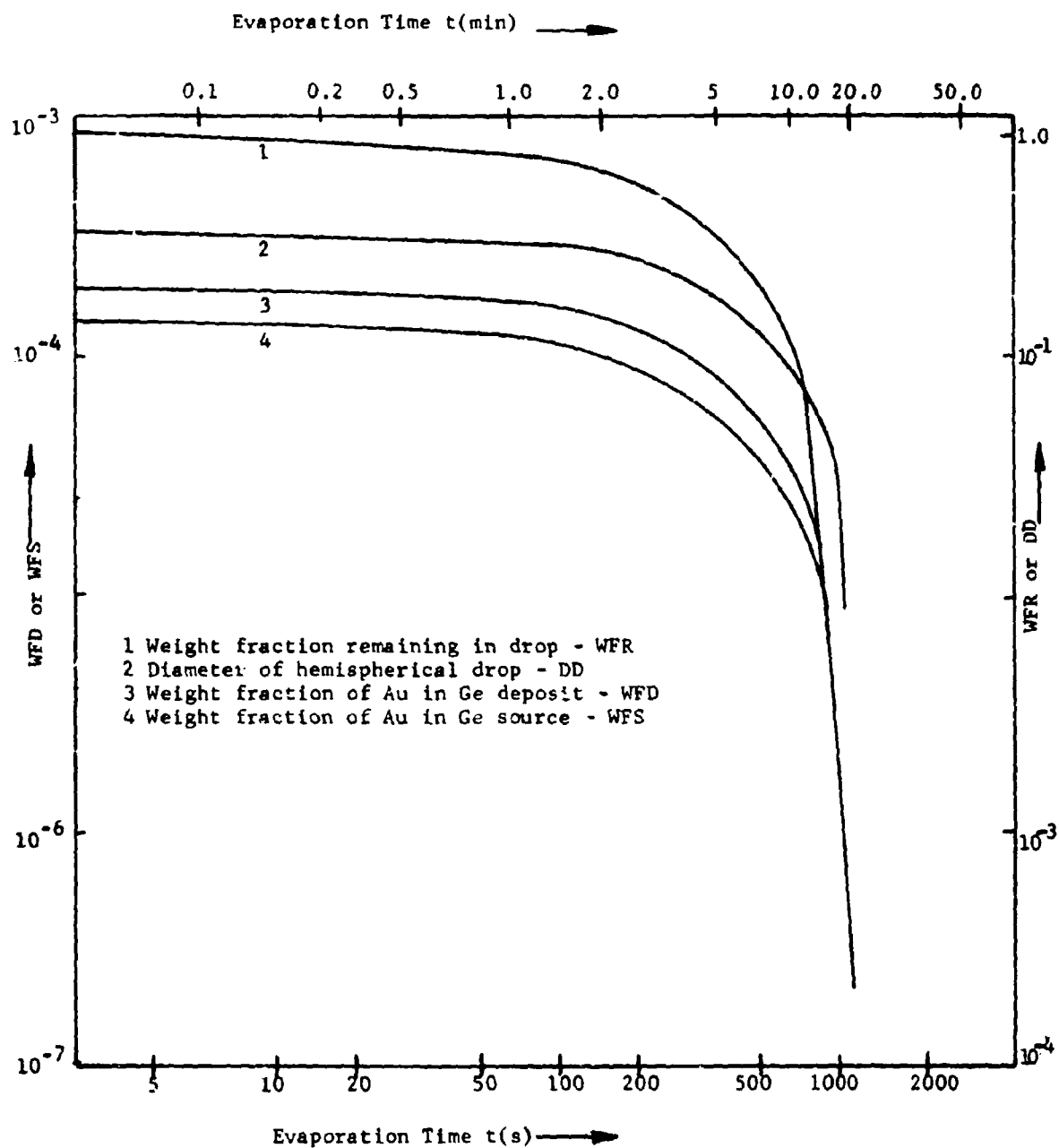


Fig. 2 Evaporation of Ge Containing 100 ppm of Au at 1800°K  
 (after Li in Ref. 11)

Other Grumman Work - In addition, we have solved equations for metal solidification combined with surface evaporation and/or chemical reaction, even for the cases with variable segregation coefficients (Ref. 19). We have further combined our grain or cell boundary model to account for the increasing rate of boundary diffusion rates. Our work here is based not on the generally accepted simple, two-material (i.e., grain or cell and boundary) model, but on a more realistic boundary model where the solute composition changes gradually and continuously from the center toward the boundary. Our model is thus a many-material boundary model. According to this model, even when the over-all or general surface evaporation is relatively minor, the boundary regions may be so preferentially evaporated that the mechanical, electrical, optical, etc. properties of the material are rapidly deteriorated (Ref. 19). Our test results (Ref. 31, Fig. 10) on vacuum-solidified nickel balls do support these conclusions (see Fig. 3).

Assuming an exponential relation between the gas solubility limit and melt temperature, we have derived an equation relating the change in specimen length, or gas bubble size and distribution in metal samples to the fraction solidified in cases where the bubbles remain immobile (Ref. 19).

#### Summary of Grumman-Developed Work

In summary, over the past few years, we have:

- 1) Derived closed-form normal freezing equations for cases where the liquidus and solidus curves are quadratic, cubic, or higher degree functions of the melt temperature.
- 2) Derived similar equations for ideal binary solutions. These equations allow the computation, with the minimum of experimentation and without the use of phase diagrams, of the solidification behavior or frozen solid concentration profiles directly from some basic thermodynamic quantities.
- 3) Developed accurate computer programs to solve numerically any solidification problems in connection with any types of liquidus and solidus curves on the phase diagram.

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Fig. 3 Surface of Vacuum-Solidified Nickel Ball, 2000x

- 4) Described uses of the above equations and programs relative to general metals solidification, single crystal growth, cellular growth, granular growth, and zone melting.
- 5) Showed why the linear normal freezing equation is so successful in the semiconductor industry but can be dangerously misleading in many metallurgical applications.
- 6) Modified the Tiller-Jackson-Rutter-Chalmers equation for normal freezing with limited liquid diffusion to account for curvatures of the liquidus and solidus lines, and showed that such modifications are necessary in many cases.
- 7) Solved the differential equation of alloy co-evaporation for the computation of complete alloy evaporation behavior, or evaporation time and optimum temperature to achieve given purification results.
8. Solved the equations for metal solidification combined with surface evaporation and/or chemical reaction, even for the cases with variable segregation coefficients.
- 9) Assessed the critical effects of trace impurities segregated during solidification at the grain or cell boundaries on the structural properties of the solidified materials.
10. Extended the generally accepted, simple, two-material grain or cell boundary model to a more realistic many-material boundary model in which the solute composition changes gradually and continuously from the center toward the boundary, and applied this model in the study of preferential diffusion, evaporation, and deterioration of grain or cell boundaries.
11. Derived equation relating the change in specimen length, or evolved gas bubble size and distribution in materials to the fraction solidified.

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